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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: J. Bednorz et al.

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Group Art Unit: ~~1105~~ / 751 /

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Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

The Commissioner of Patents and Trademarks
Washington, D.C. 20231

AFFIDAVIT UNDER 37 CFR 1.132

Sir:

I, Thomas M. Shaw, being duly sworn, do hereby depose and state:

I received a B.S. degree in Metallurgy from the University of Liverpool, Liverpool, England and a M.S. and PhD. degree in Materials Science (1981) from the University of California, Berkeley.

I have worked as a postdoctoral researcher in the Material Science Department of Cornell University from 1981-1982. I worked at Rockwell International Science Center in Thousand Oaks, California from 1982-1984 as a ceramic scientist. I have worked as a research staff member in Ceramics Science at the Thomas J. Watson Research

Center of the International Business Machines Corporation in Yorktown Heights, N.Y. from 1984 to the present.

I have worked in the fabrication of and characterization of ceramic materials of various types, including superconductors and related materials from 1984 to the present.

Attached is a resume of my publications. I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above-identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the

work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is attached herewith.

2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is attached herewith.

3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is attached herewith.

4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasso, Pergamon Press, 1969, in particular pages 159-181, a copy of which is attached herewith.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

1) Oxygen Defect K_2NiF_4 - Type Oxides: The Compounds $La_{2-x}\ Sr_xCuO_{4-x/2+\delta}$, Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).

2) The Oxygen Defect Perovskite $BaLa_4\ Cu_5\text{-}0_{13.4}$, A Metallic Conductor , C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.

3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.

4) Thermal Behaviour of Compositions in the Systems x $BaTiO_3$ + (1-x) $Ba(Ln_{0.5} B_{0.5}) O_3$, V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By: Thomas M. Shaw
Thomas M. Shaw

Sworn to before me this 14th day of December, 1998.

Sandra M. Emma
Notary Public

SANDRA M. EMMA
Notary Public, State of New York
No. 01PO4935290
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Commission Expires July 5, 2002

PUBLICATIONS T.M.SHAW

1. D.R.Clarke and T.M.Shaw, D.P.Thompson, "Direct Observation of the Polytype Periodicities in the Be-Si-O-N System.", J. Mat. Sci. 13 pages 217-219 (1978)

2. T.M. Shaw, "Transmission Electron Microscopy Analysis of Complex Nitrogen Ceramics", Proceedings of the 9th International Congress on Electron Microscopy, Toronto. Ed J.M. Sturgess (Microscopical Society of Canada, 1978). Vol. 1 Page 258.

3. D.R. Clarke and T.M. Shaw, "polytypism in Magnesium Sialon", in Processing of Crystalline Ceramics (Materials Science Research Vol. 11), Edited by H. Palmour III, R.F. Davis and T.M. Hare., Plenum press 1978.

4. T.M. Shaw and G. Thomas, "Transmission Electron Microscopy: Direct Observation of Crystal structure in Refractory ceramics",Science 202, pages 625-626 (1978)

5. O.L. Krivanek, T.M. Shaw and G. Thomas, "Imaging of Thin Intergranular Phases by High resolution Electron Microscopy", J. Appl. Phys. 50, pages 4223-4227 (1979).

6. O.L. Krivanek T.M. Shaw and G. Thomas,"The Microstructure and Distribution of Impurities in Hot-Pressed and Sintered Silicon Nitrides" J. Amer. Ceram. Soc. 62, pages 585-590 (1979)

7. T.M. Shaw O.L. Krivanek and G. Thomas, "Glass Free Grain Boundaries in Be-Si-N Ceramics", J. Amer. Ceram. Soc. 62, pages 305-306 (1979).

8. T.M. Shaw and G. Thomas,"An Electron Microscopy Study of Crystallography and Phase relationships in the Be-Si-N system", J. Solid State Chem. 33, pages 63-82 (1980).

9. T.M. Shaw and G. Thomas "The crystallization Behavior of a Mg- Si-O-N Glass " in Progress in Nitrogen ceramics, Proceedings of the NATO Advanced Study Institute, Ed F.L.Riley, Martinius Nijhoff (1983).

10. T.M. Shaw and C.B. Carter, "Faceting in Twin Boundaries in Spinel", Scripta Met. 16, pages 1431-1435 (1983).

11. P.E.D. Morgan and T.M. Shaw, "Magnetoplumbite Related Barium Aluminates", Mat. Res Bull. 18, pages 539-542 (1983).

12. P.E.D.Morgan, T.M.Shaw and E.A.Pugar "Ceramics For High Waste Loaded Commercial Radwaste disposal"In Advances in Ceramics, Vol 8, Nuclear Waste Management. Ed G.G.Wicks and W.A.Ross. Published Amer. Ceram. Soc. 1984.

13. P.E.D.Morgan, A.B.Harker, J.F.Flintoff, T.M.Shaw, and D.R.Clarke "Developments in SRP "composite" Defense Ceramic Radwaste Forms"In Advances in Ceramics, Vol 8, Nuclear Waste Management. Ed G.G.Wicks and W.A.Ross. Published Amer. Ceram. Soc. 1984.

14. T.M.Shaw, G.Thomas and R.E.Loehman "The formation and microstructure of Mg-Si-O-N Glasses" J. Amer. Ceram. Soc. Nov 1984.

15. T.M.Shaw, J.W.Steeds and D.R.Clarke "Fault Structures in CVD silicon nitride" Proceedings of M.R.S. Symposia on the Electron Microscopy of Materials. North Holland 1984.

16. T.M.Shaw and B.Pethica "The Preparation and Sintering of Homogeneous Silicon Nitride Green Compacts" J. Amer. Ceram. Soc. Vol.69 P.27 (1986).

17. T.M.Shaw "Liquid Phase Redistribution During Liquid Phase Sintering" J. Amer. Ceram. Soc. Vol.69 P.88 (1986)

18. T.M.Shaw "Movement of a drying front in a porous material" Proceedings of the M.R.S Better Ceramics through Chemistry symposium , published Elsevier 1986.

19. C.B. Carter, Z. Elgat and T.M. Shaw "First-Order Twin Boundaries parallel to the common (111) Plane in spinel. Phil. Mag. Vol 55. P.1 (1987)

20. C.B. Carter, Z. Elgat and T.M. Shaw "Lateral Twin Boundaries in Spinel. Phil. Mag Vol. 55 P.21 (1987).

21. T.M. Shaw "Drying as an Immiscible Displacement Process with Fluid Counterflow" Phys. Rev. Lett. Vol. 59, P. 1671-1674, (1987).

22. W.J. Gallagher, R.L. Sandstrom, T.R. Dinger, T.M. Shaw and D.A. Chance, "Identification and Preparation of Single Phase 90K Oxide Superconductor and Structural Determination by Lattice Imaging", Solid State Communications Vol.63 P.147 (1987).

23. R. Beyers, G. Lim, E.M. Engler, R.J. Savoy, T.M. Shaw, T.R. Dinger, W.J. Gallagher and R.L. Sandstrom "Crystallography and Microstructure of :f.Y sub 1 Ba sub 2 Cu sub 3 O sub 9-x:ef., A Perovskite-Based Superconducting Oxide" Appl. Phys. Lett Vol.50 p.1918 (1987).

24. R. Beyers, G. Lim, E.M. Engler, V.Y. Lee, M.L. Ramirez, R.J. Savoy, R.D. Jacowitz, T.M. Shaw, S. La Placa, R. Boehme , C.C. Tsuei, S.I. Park, M.W. Shafer, W.J. Gallagher "On the Relationship Between Processing, Structure, and Superconductivity in:f.Y sub 1 Ba sub 2 Cu sub 3 O sub 9-x:ef.'. Appl. Phys. Lett. 51, p 614-616 (1987)

25. R. Beyers, G. Lim, E.M. Engler, V.Y. Lee, M.L. Ramirez, R.J. Savoy, R.D. Jacowitz, T.M. Shaw, F.G. Frase, E.G.Linger, D.R. Clarke, S. La Placa, R. Boehme , C.C. Tsuei, S.I. Park, M.W. Shafer, W.J. Gallagher and G.V. Chandrashekhar. "On the Relationship Between Processing, Structure, and Superconductivity in :f.Y sub 1 Ba sub 2 Cu sub 3 O sub 9-x:ef.. Proceedings of the M.R.S symposium on Superconductivity. published Elsevier 1987.

26. T.M. Shaw "Drying Behavior in Porous Materials". Extended abstracts of the M.R.S symposium on Fractal aspects of materials published MRS 1987.

27. R. F. Cook, T.M. Shaw and P.R. Duncombe "Fracture Properties of Polycrystaline :f.Y sub 1 Ba sub 2 Cu sub 3 O sub 9-x:ef.". In Ceramic superconductors Ed. D.R. Clarke and D.W. Johonson, Published American Ceramis Society (1987).

28. T.R. McGuire, T.R. Dinger, P.J.P. Freitas, W.J. Gallagher, T.S. Plaskett, R.L. Sandstrom and T.M. Shaw, "Magnetic Properties of Y-Ba-Cu-O Superconductors" Phys. Rev B Vol.36, P.4032 (1987).

29. T.R. McGuire, F. Holtzberg, D.L. Kaiser, T.M. Shaw and S. Shinde. "Magnetic Properties of Y-Ba-Cu-O Superconductors" Proceedings of the 3M Conference. To be published J. Appl. Phys. vol 62 march (1988).

30. W. Krakow and T.M. Shaw "An Evaluation of High Resolution Electron Microscopy as a Method For Studying Y-Ba-Cu-O Superconductors", To be published J. Electron Microscopy Technique (1987).

31. W. Krakow and T.M. Shaw,"High Resolution Electron Microscopy and Electron Diffraction of :f.Y sub 1 Ba sub 2 Cu sub 3 O sub 7-x:ef.". Proceedings of the MRS Fall Symposium on Superconductivity published Elsevier 1987.

32. T.M. Shaw, S.A. Shivashankar, S.J. La Placa, J.J. Cuomo, T.R. McGuire R.A. Roy, K.H. Kelleher and D.S. Yee "Incommensurate structure in the Bi-Sr-Ca-Cu-O 80K Superconductor" Phys. Rev. B 37(16), 9856 (1988).

33. T.R. McGuire, S.A. Shivashankar, S.J. La Placa, G.V. Chandrasheka, R.F. Boehme, T.M. Shaw, D.S. Yee, M.W. Shafer, and J.J. Cuomo "Superconductivity in Bi-Sr-Ca-Cu-O" J. Appl. Phys. Vol 64 1988.

34. A.C. Nunes, S.J. Pickart, L. Crow and Goyette (University of Rhode Island) T.R. McGuire, S. Shinde and T.M. Shaw (IBM) "Neutron depolarization by a High Tc Superconductor" To be published J. Appl. Phys. Vol 64 1988.

35. R. Beyers and T.M. Shaw "The Structure of 123 and its Derivatives", Solid State Phys. Vol. 42 P.135-212 1989.

36. T.M. Shaw S. Shinde, D. Dimos, R.F. Cook, P.R. Duncombe, and C. Kroll" "The Effect of Grain Size on Microstructure and Stress Relaxation in Polycrystalline 123", J. Mat. Res. Vol.4 P.248-256, 1989.

37. D.R. Clarke, T.M. Shaw and D. Dimos "Issues in the Processing of Cuperate Ceramic Superconductors" J. Amer. Ceram. Soc 72, 1103 (1989).

38. G. Burns, M. K. Crawford, F. H. Dacol, E. M. McCarron III, and T. M. Shaw, Phonons in :f.CaCuO sub 2 ,:ef. Phys. Rev. B **40**, 6717 (1989).

39. T.M. Shaw, D. Dimos, P.E. Batson, A.G. Schrott, D.R. Clarke and P.R. Duncombe, "Carbon Retention in :f.'Y' <'Ba' sub 2> <'Cu' sub 3>'O'sub <7-delta>':ef. and its Effect on the Superconducting Transition," J. Mat. Res. 5(6), 1176 (1990).

40. S.L. Shinde and T.M. Shaw, "Considerations for Improved Polycrystalline Cuprate Superconductors," Page 579 in Superconductivity and Ceramic Superconductors, Eds. K.M Nair and E.A. Giess, 13, Ceramics Trans., Published Amer. Ceram. Soc.

41. J.F. Bringley, B.A. Scott, S.J. La Placa, R.F. Boehme, T.M. Shaw, M.W. McElfresh and S.S. Trail, "Synthesis of :f.'LaCuO' sub <3-delta>:ef. a new Defect Perovskite with Variable Copper Valence from +2 to +3." Nature, **347**, 263-265 (1990).

42. B.S. Berry, W.C. Pritchet and T.M. Shaw, "Anelastic Measurements of Atomic Mobility in the Superconductor :f.'Y' <'Ba' sub 2> <'Cu' sub 3>'O'sub <7-delta>':ef.," Defect and Diffusion Forum 1990.

43. M.K. Crawford, G. Burns, E.M. McCarron, G.V. Chandrashekhar, W.E. Farneth, and T.M. Shaw, "Infrared and Raman Spectroscopy of Phonons in :f.(Nd/Pr) sub 2 CuO sub 4:ef. :f.(Ca

sub 0.86 Sr sub 0.14)CaO sub 2:ef.," Materials Research Society Proceedings, 169, 1013 (1990).

44. P.E. Batson, T.M. Shaw, D.Dimos and P.R. Duncombe "Participation of Carbon in the Electronic-Structure of YBa2Cu3O7-Delta". Physical Review B-Condensed Matter 1991, Vol 43, Iss 7, pp 6236-6238

45. T.K. Worthington, E. Olsson, C.S. Nichols, T.M. Shaw and D.R. Clarke "Observation of a Vortex-Glass Phase in Polycrystalline YBa2Cu3O7-X in a Magnetic-Field" Physical Review B-Condensed Matter Vol 43, Iss 13, pp 538-543, (1991).

46. T.M. Shaw and P.R. Duncombe, "Forces Between Aluminum Oxide Grains in a Silicate Melt and their Effect on Grain Boundary Wetting," J. Amer. Ceram. Soc, 74, P.2495, (1991).

47. "Synthesis and Processing of Ceramics: Scientific Issues," MRS Proceedings Vol. 249, Editors W.E. Rhine, T.M. Shaw R.J Gottschall and Y. Chen. Published (1992).

48. M. D&ae.umling, L.E.Levine and T.M.Shaw, ":ef.T sub c:ef., :f.H sub c2:ef., and Oxygen Ordering in Quenched Oxygen Deficient YBa&sub2.Cu&sub3.:f.O sub < 7 -dlt > :ef. " Advances in Cryogenic Engineering (Materials), Published (1992).

49. T. Frey, C.C. Chi, C.C.Tsuei, T.M. Shaw and G. Trafas, "RHEED-controlled Unit-Cell by Unit-Cell Layer-Growth of High-Tc Cuperate Films with Laser Ablation Technique,"MRS Proceedings, Vol.275 P. 61, (1992).

50. C.C.Tsuei, T. Frey, C.C. Chi, T.M. Shaw, D.T. Shaw and M.K. Wu, "The Making of High-Tc Layered Superconductors," Proceedings of the Buffalo conference on Superconductivity and its Applications (1992).

51. M.Y. Chern, A. Gupta, B.W. Hussey and T.M. Shaw, "RHEED Intensity Monitored Homoepitaxial Growth of :f.'SrTiO' sub 3:ef. Buffer Layer by Pulsed Laser Deposition," J. Vac. Sci. Technol. A. 11, 637 (1993).

52. M. Daumling, P.R. Duncombe, K.H. Kelleher, R.A. Figat and T.M. Shaw, "upper Critical-Field of Gold-Doped YBa&sub2.Cu&sub3.:f.O sub < 7 -dlt > :ef.," Phys. Rev. B 47, P. 6177, (1993).

53. T.M. Shaw "A Model for the Effect of Powder Packing on the Driving Force For Liquid Phase Sintering," J. Amer. Ceram. Soc 76, P.664, (1993).

54. D.R. Clarke T.M. Shaw, A.P. Philipse and R.G. Horn "On a possible Electrical Double layer Contribution to the Equilibrium Thickness of Intergranular Glass Phases in Polycrystalline Ceramics" to be published, Journal of the American Ceramics Society (1993).

55. T. Frey, C.C. Chi, C.C.Tsuei, T.M. Shaw and F. Bozso "THe Effect of Atomic Oxygen on the Initial Growth Mode in Thin Epitaxial Cuprate Films", Phys. Rev. B.49,P. 3483,(1994).

56. A.Gupta, B.W. Hussey, T.M. Shaw, R.F. Saraf, J.F. Bringley and B.A. Scott, "Growth of Thin Films Of the Defect Perovskite :f.'LaCuO' sub <3-delta>:ef. by Pulsed Laser Ablation",Solid State Commu.,108, P.202, (1994).

57. A.D. Kent, T.M. Shaw and S. von Molnar, "Growth of High Aspect Ratio Nanometer Scale Magnets Using Chemical Vapor Deposition and Scanning Tunneling Microscope Techniques," Science, 262, P.1249 (1993).

58. A. Gupta, B. W. Hussey, T. M. Shaw, A. M. Guloy, M. Y. Chern, R. F. Saraf, and B. A. Scott, "Layer-by-Layer Growth of Thin Films of the Infinite-Layer Compounds: &sco. and &cco.", J. Solid State Chem. 112, P. 113, (1994).

59. T.M. Shaw, A. Gupta, B.W. Hussey, P.E. Batson, B.A. Scott and R.B. Laibowitz, " Atomic Scale Oxide Superlattices Grown by RHEED Controlled Pulsed Laser Deposition," , J. Mat. Res.,9,P.2566, (1994).

60. A. Gupta, T.M. Shaw, M.Y. Chern, B.W. Hussey, A.M. Guloy and B.A. Scott, " Reflection High-Energy Electron Diffraction Monitored Growth of Infinite-Layer &cco./&sco. Thin Film Heteostructures" To be published Phys. Rev. B.

61. J. Drennan, D. R. Clarke, R.H.J. Hannink and T.M. Shaw, "Effect of Oxygen Partial Pressure on the Microstructure of Mg_PSZ with Strontia and Silica Additions", J. Amer. Ceram. Soc. 77, P.2001, (1994).

62. A.Grill, W. Kane, D. Beach, R. Laibowitz and T.M. Shaw., "Preparation of Strontium Titanate Films by MOCVD", To be published J. Integrated ferroelectrics (1994).

63. D.B. Beach, R.B. Laibowitz, T.M. Shaw, A. Grill, and W.F. Kane, "Thickness Dependent Dielectric Properties of Sol Gel prepared Lead-Lanthanum TiTanate Films. To Be published, Journal of Integrated Ferroelectrics.

64. J.R. Kirtley, P. Chaudhari, M.B. Ketchen, N. Khare, S.Y. Lin and T.M. Shaw, "Scannning SQUID TEST of the Symmetry of the High-Tc Superconducting Order Parameter" To be published..... (1994)

65. C.C. Tsuei, J.R. Kirtley, C.C. Chi, L.S. Yu-Jahnes, A. Gupta, T.M. Shaw, J.Z. Sun and M.B. Ketchen, Pairing Symmetry and Flux Quantization in a Tri-Crytal Superconducting Ring of YBa&sub2.Cu&sub3.:f.O sub < 7 -dlt > :ef.", To be published.... (1994).